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Anne Lewis
University of Northern Iowa

Christopher Cramer
University of Minnesota

See next page for additional authors

Author
Anne Lewis, Christopher Cramer, and John Bumpus

The Redox Potential of DDT: An Environmental Perspective

Anne Lewis[1], Christopher Cramer[2], and John Bumpus[1]

[1]Department of Chemistry and the Environmental Sciences Program
University of Northern Iowa
Cedar Falls, Iowa 50614

[2]Department of Chemistry
University of Minnesota
Minneapolis, Minnesota

Abstract

Due to their low water solubility, the reduction potentials of DDT and dicofol are difficult to determine experimentally. Through computational methods, we calculated the one and two electron reduction potentials for DDT as 0.51 V and 0.67 V, respectively, and those for dicofol were 0.50 V and 0.74 V. This study is significant because we are able to calculate reliable redox potentials that may be utilized to predict chemical behavior and degradation pathways of environmental pollutants. To assess the accuracy of theoretical chemistry, we compared experimental and computational data and examined whether our calculated redox potentials fit with the known redox behavior of DDT.

Introduction

DDT (dichlorodiphenyltrichloroethane), a very effective insecticide, was used extensively from 1940 until 1973, and because of its harmful environmental effects, most use of DDT has been banned (1). DDT, as well as a number of DDT analogs and degradation products may take many years to degrade in soil, and because of their low water solubility (most estimates of the water solubility of DDT range between 1 and 5 micrograms per liter) (2) and high octanol-water partition coefficient, they tend to accumulate in the adipose tissues of fish, birds, humans,

and other organisms occupying higher trophic levels (3). DDT appears to interfere with the reproductive ability of birds, and recent evidence suggests that DDT and/or its immediate degradation products may function as hormone disruptors (1).

Reduction potentials are useful electrochemical constants that may be used to predict the reactivity, behavior, and degradation pathways of chemical compounds. Reduction potentials can be experimentally determined for many water-soluble molecules. However, there exist many compounds that are not very soluble in water, and the determination of the redox potentials of such compounds by standard procedures is, at best, difficult. This is the case for DDT, its immediate degradation products, and its analog, dicofol (Fig. 1) (1, 3, 4).

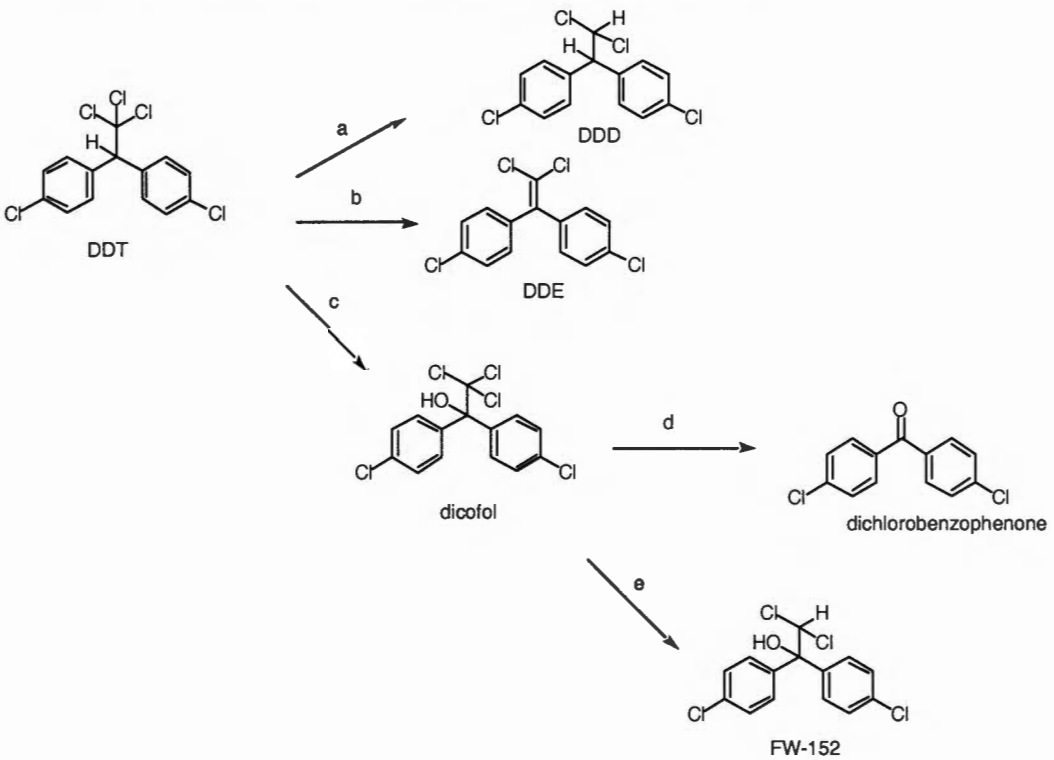
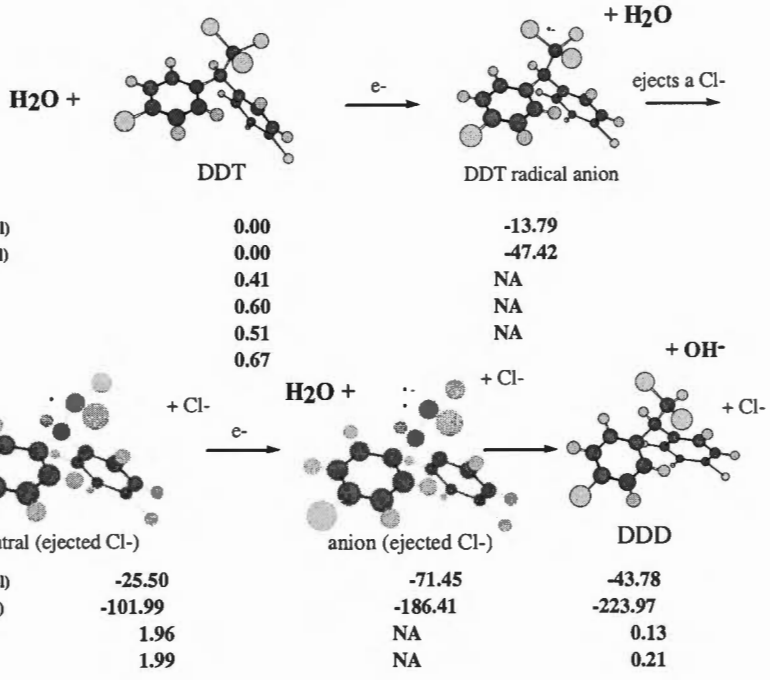


Fig. 1. Degradation products of DDT and dicofol.
(a) DDT undergoes reductive dechlorination. (b) DDT undergoes dehydrohalogenation. (c) DDT is hydroxylated. (d) Dicofol is oxidized. (e) Dicofol undergoes reductive dechlorination.

To our knowledge, the redox potential of DDT has not been measured, and although direct experimental determination of physical and chemical constants is preferred, a computational approach can provide valuable information and a reliable estimation of such parameters (5). Recently, we published procedures detailing a computational approach used to calculate the redox potential of DDT and dicofol. Redox potentials of 0.51 V and 0.67 V for the one and two electron reduction potentials, respectively, of DDT were determined. The two-electron reduction of DDT results in formation of DDD (Fig. 2).

Fig. 2. Mechanism of Reductive Dechlorination of DDT.



relative G(gas)(kCal/mol)	0.00	-13.79	
relative G(aq) (kCal/mol)	0.00	-47.42	
vertical EA (V)	0.41	NA	
adiabatic EA (V)	0.60	NA	
1 e- E ° (V)	0.51	NA	
2 e- E ° (V)	0.67		
relative G(gas)(kCal/mol)	-25.50	-71.45	-43.78
relative G(aq)(kCal/mol)	-101.99	-186.41	-223.97
vertical EA (V)	1.96	NA	0.13
adiabatic EA (V)	1.99	NA	0.21

Fig. 2. Thermochemical data from Table 1 were used to calculate chemical parameters such as optimized geometries, vertical and adiabatic electron affinities, and one and two electron redox potentials for DDT and DDD.

Redox potentials of 0.50 V and 0.74 V for the one and two electron reduction potentials, respectively, of dicofol were also determined. The two-electron reduction of dicofol results in the formation of FW-152 (Fig. 3).

Fig. 3. Mechanism of Reductive Dechlorination of Dicofol

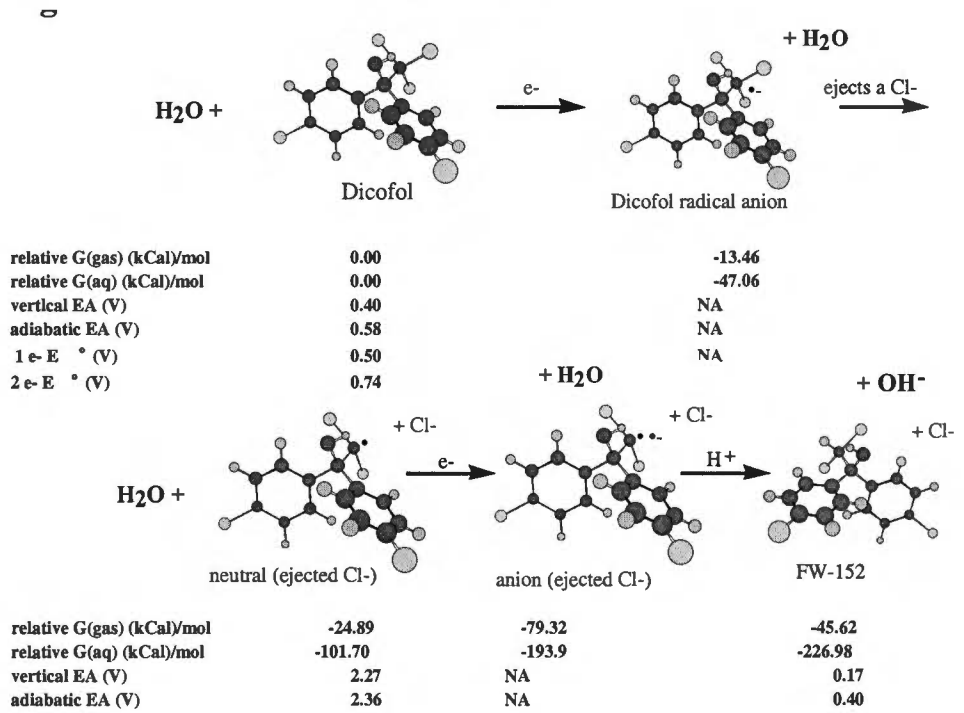


Fig. 3. Thermochemical data for dicofol were used to calculate chemical parameters such as optimized geometries, vertical and adiabatic electron affinities, and one and two electron redox potentials for dicofol and FW-152.

Here, we provide an assessment concerning the reliability of these calculated redox potentials, and we discuss them in context of the known redox behavior of DDT and its degradation products. Furthermore, this information assists us in estimating the redox potential of DDD.

Methods

The one and two-electron reduction potentials for DDT and dicofol were computed using Gaussian 98, a suite of electronic structure programs that employ different levels of theory to compute various thermochemcial quantities. Insofar as heats of formation, entropies, and solvation free energies are not known for DDT or its degradation products, theoretical quantum chemistry methods were employed to calculate such quantities using a thermochemical cycle (Fig. 4-5) (7, 8).

$$\begin{array}{ccccccc} & & & \overset{\Delta G^{o}_{(g)}}{\rightarrow} & & & \\ DDT_{(g)} & + & e^{-}_{(g)} & & DDX_{(g)} & + & Cl^{-}_{(g)} \\ \downarrow \Delta G^{o}_{S}(DDT) & & \downarrow \Delta G^{o} = 0 & & \downarrow \Delta G^{o}_{S}(DDX) & & \downarrow \Delta G^{o}_{S}(Cl^{-}) \\ & & & \overset{\Delta G^{o}_{(1e)}}{\rightarrow} & & & \\ DDT_{(aq)} & + & e^{-}_{(g)} & & DDX_{(aq)} & + & Cl^{-}_{(aq)} \end{array}$$

Fig. 4. Thermodynamic cycle for the determination of the absolute 1-electron reduction potential of DDT (6).

$$\begin{array}{ccccccccc} & & & & \overset{\Delta G^{o}_{(g)}}{\rightarrow} & & & & \\ DDT_{(g)} & + & H^{+}_{(g)} & + & 2e^{-}_{(g)} & DDD_{(g)} & + & Cl^{-}_{(g)} & \\ \downarrow \Delta G^{o}_{S}(DDT) & & \downarrow \Delta G^{o}_{S}(H^{+}) & & \downarrow \Delta G^{o} = 0 & \downarrow \Delta G^{o}_{S}(DDD) & & \downarrow \Delta G^{o}(Cl^{-}) & \\ & & & & \overset{\Delta G^{o}_{(2e)}}{\rightarrow} & & & & \\ DDT_{(aq)} & + & H^{+}_{(aq)} & + & 2e^{-}_{(g)} & DDD_{(aq)} & + & Cl^{-}_{(aq)} & \end{array}$$

Fig. 5. Thermodynamic cycle for the determination of the absolute 2-electron reduction potential of DDT (6).

Such cycles are useful because they permit different, specialized levels of theory to be applied to gas-phase processes and solvation processes. Based on a balancing of efficiency and accuracy,

density functional theory (DFT) was selected as the electronic structure theory best suited for DDT given its size. DFT calculates molecular energetics taking the optimized electron density as its fundamental variable (7, 9). We selected a hybrid functional (which combines Hartree-Fock theory with DFT) called B3LYP (10-13). In addition, the 6-31G* basis set was selected to carry out the electronic structure calculations (7, 14).

$$DDT_{(aq)} + e^-_{(g)} \rightarrow DDX_{(aq)} + Cl^-_{(aq)} \qquad (1)$$

$$DDT_{(aq)} + H^+_{(aq)} + 2e^-_{(g)} \rightarrow DDD_{(aq)} + Cl^-_{(aq)} \qquad (2)$$

The B3LYP/6-31G* level of theory was used specifically to predict molecular geometries and vibrational frequencies, from which ideal-gas partition functions can be computed. However, electronic energies computed at the B3LYP/6-31G* level are subject to improvement; therefore "single point" calculations (i.e., without reoptimization of the geometry) at the B3LYP/6-311+G* level were undertaken. The latter level of theory provides a better prediction of the electronic energy by using an improved basis set. To compute the free energies of solvation all products and reactants, the solvation model SM5.42R/BPW91/6-31G* was used (15). This model treats the surrounding solvent (water) as a homogenous dielectric medium with a reaction field generated by the charge distribution of the solute. After computation of the different components at the B3LYP/6-31G*, B3LYP/6-311+G*, and SM5.42R/BPW91/6-31G levels, the free energy of reaction in aqueous solution, ΔG_s° was calculated.

$$\Delta G_s^\circ = \Delta G_{(g)}^\circ + \Delta\Delta G_s^\circ \qquad (3)$$

where $\Delta G_{(g)}^\circ$ = the computed free-energy change in the gas phase, and $\Delta\Delta G_s^\circ$ = differential solvation free energy of the products and reactants.

The absolute ΔG_s° was then converted to a relative ΔG° by adding the absolute cell potential for the reference normal hydrogen electrode (4.36 V). The relative cell potential was then determined.

$$\Delta G^{o'} = -nFE^{o} \qquad (4)$$

where n is the number of electrons transferred, F is the Faraday constant, and E^{o}=cell potential (Volts).

Computational methods typically assume a 1 M standard state for aqueous solutes; however, under experimental conditions, aqueous reductive dechlorinations are buffered to a pH of 7 and a chloride ion concentration of 10^{-3} M. To convert to this different standard state, we may use

$$\Delta G^{o} = \Delta G^{o'} + RT \ln [Q^{o}/Q^{o'}] \quad (5)$$

where Q is reaction quotient, superscript ^{o} indicates pH = 7 and 10^{-3} M Cl^{-}, and superscript $^{o'}$ indicates all aqueous concentrations at 1 M. For a more detailed interpretation, refer to (6).

Discussion

The gas phase data from B3LYP/6-311+G* and SM5.42R/BPW91/6-31G theory levels for the reductive dechlorination of DDT to DDD are contained in Table 1.

***Table 1. Computed 298 K Gas phase Thermochemical Data for use with Equations 1 & 2.**

Species	E_{elec}	Uo	H_{298}	G^{o}_{298}	ΔG^{o}_{S}
e^{-}	0.000 00	0.000 00	0.009 88	-0.000 04	N/a
H^{+}	0.000 00	0.000 00	0.009 88	-0.041 81	-0.417 66
Cl^{-}	-460.303727	-460.303 73	-460.301 37	-460.302 31	-0.119 73
DDT	-2840.13786	-2839.94728	-2839.92881	-2839.99554	-0.001 95
DDX	-2379.87231	-2379.68479	-2379.66739	-2379.73386	-0.001 10
DDD	-2380.53053	-2380.32966	-2380.31233	-2380.37716	-0.002 75

Gas phase data from B3LYP/6-311+G* calculations with 1 mol per 24.5 L and ion convention standard state; solvation free energies from SM5.42R/BPW91/6-31G calculations including concentration to 1 M standard state *(6).

These values were used in equations 1 and 2 for DDT and dicofol to determine the one and two electron reduction potentials in Figs. 2 and 3. The one and two electron redox potentials for DDT were 0.51 V and 0.67 V, respectively, and those for dicofol were 0.50 V and 0.74 V, respectively. Although there currently exist no experimental redox data for DDT for comparison, a number of other computational values complement experimental data, thus establishing the validity and accuracy of computational methods used. A study by Patterson et al (16) compared the experimental data with computational data (Table 2) for the reductive dechlorination of hexachloroethane (HCA).

***Table 2. Experimental and Theoretical Thermochemistry of Processes Relevant to Reductive Dechlorination of Hexachloroethane.**

Process	Phase	Thermochemcial quantity	Expt	BPW91
(A) $Cl\bullet + e^- \rightarrow Cl^-$	gas	$-\Delta H_o$	3.61	3.64
	aqueous	$E_1^{\varnothing,}$	2.54	2.54
(B)HCA+ $2e^- + H^+ \rightarrow$ PCA+Cl^-	gas	$\Delta G^o_{(g)}$	-18.54	-18.55
	aqueous	$E_1^{\varnothing,}$	0.67	0.69
(C) HCA + $2e^- \rightarrow$ PCE + $2Cl^-$	gas	$\Delta G^o_{(g)}$	-4.37	-4.61
	aqueous	$E_2^{\varnothing,}$	1.15	1.28
(D) HCA + e- $\rightarrow$ PCA$\bullet$ +Cl^-	gas	$\Delta G^o_{(g)}$	-1.16	-1.45
	aqueous	$E_1^{\varnothing,}$	0.11	0.44

Reduction potentials are in volts; all other quantities are in electron volts. *(16).

The experimental and theoretical two-electron redox potentials in process (B) differ by only 0.02 V, and other theoretical data in the table compare favorably with the experimental data, thus indicating the accuracy of the SM5.42R/BPW91/6-31G theory level. Because the mechanism of the two-electron reduction of HCA is comparable to that of DDT, we suggest that the theoretical calculations accurately depict the redox potentials of DDT and dicofol.

The fact that the calculated redox potentials of DDT are consistent with its observed behavior in laboratory experiments and in the environment is further support of the validity of

our theoretical methods. Redox potentials of such pollutants as DDT and dicofol allow us to predict degradative pathways in the presence of certain redox pairs. If the redox potential of a redox pair is known, one can predict which member of the pair will be oxidized and which will be reduced during its reaction with another redox pair. The standard redox potential for the Fe^{++}/Fe^{+++} redox pair is 0.77 V. Because of its relatively high positive redox potential, reduction of DDT to DDD would not be especially favored in the prescence of Fe^{++}/Fe^{+++} under standard conditions. Glass reported partial but certainly not extensive conversion of DDT to DDD at high pH in the presence of ferrous iron during seven days of incubation (17). It is expected that some reduction of DDT to DDD would be observed under these conditions. However, because the redox potential of the Fe^{++}/Fe^{+++} redox pair is substantially greater than that calculated for the DDT/DDD redox pair, it is also expected that, as observed, reduction of DDT to DDD would not be extensive.

It is known that chelation of the Fe^{++}/Fe^{+++} redox pair lowers its redox potential. For example, the redox potential of the Fe^{++}/Fe^{+++} redox pair in hemoglobin is 0.17 V and a very low –0.432 V in ferredoxin. Zoro et al showed that the Fe^{++}/Fe^{+++} redox pair of hematin was able to mediate substantial reduction of DDT to DDD (18). Although sodium dithionite or ferrous sulfate was used to decrease the electrode potential (E_h) of the solution, reduction of DDT was dependent on the presence of the Fe^{++}/Fe^{+++} hematin.

In another investigation, Kitamura et al have shown that the Fe^{++}/Fe^{+++} redox pair in hemoglobin and hematin is able to mediate reduction of DDT to DDD in the presence of an electron donor such as a reduced flavin (19). Again, this demonstrates that reduction of DDT to DDD occurs in the presence of chelated complexes of the Fe^{++}/Fe^{+++} redox pair, which is due to their decreased redox potentials.

Although the redox potential of DDD is yet to be determined, it is known that DDD is the major degradation product of DDT and is more persistent in the environment (3, 20). Because it tends to accumulate more than DDT, we would expect DDD to have a two-electron redox potential lower than that of DDT. It is also of interest to compare the one and two electron redox potentials of DDT and dicofol. The similarities in their theoretical redox potentials support previous studies that such similar molecules degrade under similar reducing conditions (4).

Conclusion

Theoretical procedures were used to predict previously unknown one and two electron reduction potentials for pesticides DDT and dicofol. The accuracy of such computational methods was discussed based on our comparisons of experimental and theoretical data for the reductive dechlorination of HCA and previous studies involving the reduction of DDT with chelated Fe^{++}/Fe^{+++} and chelates of Fe^{++}/Fe^{+++}. Based on this information, we were able to comment on the reliability of the computational approach, as well as to form predictions about the redox potential of DDD.

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